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(54) RESINOUS MOLDING POWDERS

(71) We, TRW, INC., a corporation organised under the laws of the State of Ohio, United States of America, of One Space Park, Redondo Beach, California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel fast curing elastomeric molding powders. These elastomers are obtained in or communited to a desired particle size, and the resulting elastomeric particles may be molded according to procedures known in the art and hardened by heat.

The thermosetting, cross-linked, cyclized polydiene resin derived from the molding powders of this invention belong to the family of resins characterized by the cross-linked, linearly-extended chains of condensed cycloaliphatic groups discussed in copending Patent Applications No. 9398/67 (Serial No. 1,193,301); No. 30037/67 (Serial No. 1,195,565); No. 30589/67 (Serial No. 1,195,566); and No. 35781/67 (Serial No. 1,194,723). It is to be understood that the polyester copolymers, the polyether copolymers, the hydrocarbon copolymers, and the internally plasticized forms described in these co-pending applications may be employed in the practice of this invention as well as the described chain extenders and peroxide free radical initiators enumerated therein.

In general, the molding powders according to this invention, are produced by comminution of the reaction product of a polyfunctional polydiene prepolymer having mainly pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain with a polyfunctional chain extender capable of reacting with the functional groups of the polydiene and a peroxide free radical initiator capable of promoting the production of a hard resin on the subsequent application of heat.

Polydiene prepolymers used in production of the thermosetting molding powders of this invention should have predominantly pendant vinyl groups on alternate carbon atoms of the backbone carbon chain, preferably constituting at least 80% of the olefinic unsaturation, and should preferably have a molecular weight from about 500 to about 3000. The preferred polydiene is 1,2-polybutadiene, although 3,4-polyisoprene is also suitable and the expression "vinyl group" should therefore be understood to include α-methylvinyl. Difunctional compounds characterized by terminal substitution are preferred, however, other polyfunctional prepolymers having functional groups located at opposite ends of the molecule, but not necessarily the terminal positions, may be used. While a dihydroxy substituted prepolymer is generally preferred, mainly from the standpoint of ease of reactability, a dicarboxy substituted compound or other polydienic prepolymer having chemically functional groups preferably terminally positioned will also be satisfactory.

Selection of a suitable organic chain extender is dependent upon the functional groups on the prepolymers. Where the functional groups on the prepolymers are hydroxyl, chain extenders should be diisocyanates, diacid halides, diacids, or diesters. Where the functional groups on the prepolymers are carboxyl, the chain extenders should be diepoxides, diimines, diols, and diaziridines. The aliphatic or aromatic organic chain extenders are preferably difunctional, but may contain more than two functional groups.

Important to the curing steps of the process are the peroxide free radical initiators. These peroxide initiators are instrumental in the production of a hard resin upon the application of heat. The peroxide initiator

is introduced into the initial mixture along with the polydiene prepolymer and the organic chain extender whereupon it becomes molecularly dispersed throughout the ensuing elastomeric polymer. Upon the application of heat in the final molding step, the peroxide initiator decomposes to provide free radicals which are believed to force the pendant vinyl groups to join to form cross-linked, condensed cycloaliphatic chains.

In preparing these resins, the polyfunctional organic chain extender should be mixed in an approximately stoichiometric amount to the polydiene prepolymer. Adjustments are necessary when other ingredients such as copolymeric prepolymers or internal plasticizers are employed, but approximately stoichiometric amounts of the organic chain extender with respect to the prepolymeric ingredients is the preferred quantity. The peroxide is generally employed in an amount within the range of 0.5% to 10% by weight of the prepolymer, and preferably within the range of 2% to 6%. It will be appreciated that larger or smaller amounts of the peroxide may be employed and that the optimum amount is dependent upon, among other things, the particular peroxide initiator used, the polydiene prepolymer employed, and the chain extender selected for the reaction.

After the ingredients have been mixed, the polymeric liquid should desirably be degassed in vacuum to remove entrapped air and volatile impurities. A chain extending reaction proceeds at room temperature or moderately elevated temperatures to produce an elastomeric intermediate material characterized by having the peroxide free radical initiator molecularly dispersed throughout. The chain extension reaction may be catalyzed to reduce reaction temperature or time by catalytic agents which are standard art, providing they do not interfere with the subsequent hardening step. While the polymer is in this elastomeric state it may be easily handled as a molding powder, and fabricated. When a desired article has been formed, the elastomeric polymer is heated in the range of 150°F to 400°F whereupon hardening takes place to produce a tough, stiff, transparent plastic.

Molding powders of this invention may be prepared by a variety of expedients. One means of comminution employs grinding or grating the intermediate elastomeric stage at room temperature. To reduce the difficulties of controlling the particle size during comminution of the rubbery material, the material may be frozen to a hard consistency using liquid nitrogen and then subjected to comminution by grinding, grating, or cutting.

Another means for preparing the molding powder consists of extruding reacting mixtures of the resin ingredients, either in the presence or absence of fillers, through a temperature regulated device having small orifices. The temperature control permits the first stage reaction to ocur so that the elastomeric material is formed by the time the material appears at the end of the orifice passage. The device is equipped with a cutter that chops off small sections of the cured elastomeric-stage material of desired size.

Still another means of preparing the molding powders consists of spraying a liquid mixture of the starting ingredients, concurrently with a warm gas such as air, through spray nozzles or discs into a drying chamber, for example a spray dryer may be used. The temperature of the gas and the drying chamber is controlled so that the first stage reaction or chain extension reaction occurs to produce a powder of elastomeric material. When desired, fillers can be incorporated in the liquid starting ingredients prior to spraying. Of course, the usual precautions must be exercised in conducting this operation, e.g., care should be taken to make sure that the particle size of the filler is sufficiently small to avoid clogging the spray nozzle and to permit a relatively free flow of the materials.

The particle size range may vary widely and, in general, is governed mainly by the process equipment and the product to be formed. The lower limit of particle size is kept sufficiently large to avoid dusting, and the upper limit is sufficiently small to avoid binding when loading the mold.

In the fabrication of resin articles by compression molding, the elastomeric resin powders were comminuted to the desired size, and placed in a heated mold. Heat and pressure were simultaneously applied to the resin powder, and a hard, rigid resin article was produced thereby. It has been determined that it is desirable to keep molding temperatures below 140° to 150°C, since above these temperatures the exothermic reaction becomes so vigorous and rapid that it cannot be controlled. Fillers can be used to reduce the degree of the exothermic reaction. Usually temperatures above about 100°C are necessary in order to give the resin a reasonable curing time, however, it should be understood that these molding temperatures are suggestions only and are subject to variation depending on the thickness of the molded part, the fillers used, and the resin composition. The pressures applied are also subject to the same process and composition considerations.

If a more rapid reaction is desired, a thickening agent such as trimethylol propane may be added to the prepolymer mixture. Trimethylol propane provides more functional hydroxyl groups for reaction with the diisocyanate. The result of the increased

functionality is enhancement of the thermosetting characteristics.

To achieve special properties in the final product, fillers may be added to the liquid prepolymer prior to formation of the elastomeric stage. To permit better mixing, toluene, or preferably styrene, may be added to the liquid prepolymer mixture. If toluene is employed as the thinning agent, the mixture must be allowed to stand until the toluene has evaporated. If styrene is employed as the thinning agent, no removal step is necessary as it becomes an internal plasticizer. By the addition of these thinning agents, the filling powder is thoroughly wetted by the liquid prepolymer, and a more homogeneous mixture is effected. This mixture is allowed to react to form the filler-containing intermediate elastomeric stage and is subsequently comminuted to homogeneous powder form ready for molding. An alternative approach to the molding process may be accomplished by mixing the fillers with the intermediate elastomeric stage powders to form a heterogeneous molding powder.

Filler powders to be used may be drawn from a wide range of materials. Suitable materials may be selected from synthetic fabrics, carbon, asbestos, silica, glass, silicates, metals, metallic oxides, or plastics materials. Chemical inertness of the filler with respect to the surrounding resin matrix and the environment in which the product will be used are prime factors for consideration when selecting the filler.

A filler of special interest is the final hard resin itself. The resin according to this invention is reacted to the final hard product and comminuted to desired particle sizes. These hard resin particles are then employed as filler material for molding processes according to practices known in the art as set forth above. Since resins according to this invention have outstanding resistance to attack by chemicals such as halogenated solvents, organic and inorganic acids, strong alkalies, and nitrogen oxide compounds, several advantages attend the application of this practice. For example, because filler material which will have the same final chemical composition as the matrix is employed, a homogeneous final product is obtained. This practice is particularly advantageous where it would not be desirable to sacrifice the chemical stability of bushings, bearings, gaskets, O-rings and the like by the introduction of foreign filler material. Further advantages of the resin filled resin are found in the processing techniques where shrinkage is decreased proportionally with increasing amounts of the final resin powder used. Less heat is required for the mold cure since the final cured resin powder acts as a heat sink to provide a more or less even temperature profile throughout the molded article and only a little more than the amount of heat to cure the resin matrix is necessary.

Molding powders according to this invention provide a fast curing thermosetting plastic with high heat distortion temperatures. The molded products exhibit outstanding resistance to chemical attack by water, solvents, or oxidizing acids, and a judicious selection of filler powders permits the fabrication of parts having a wide range of electrical, thermal, and mechanical properties.

WHAT WE CLAIM IS:—

1. A molding powder comprising elastomeric particles which comprise the reaction product of (a) a polyfunctional polydiene prepolymer having mainly pendant vinyl groups on alternate carbon atoms of an elongate backbone carbon chain with (b) a polyfunctional chain extender capable of reacting with the functional groups of the polydiene prepolymer, the reaction product having a peroxide free-radical initiator molecularly disposed therethrough which is capable of promoting the production of a hard resin on the subsequent application of heat.

2. A molding powder according to Claim 1 wherein the polyfunctional polydiene is dihydroxy, 1,2-polybutadiene or dihydroxy 3,4-polyisoprene.

3. A molding powder according to Claim 2 wherein the polyfunctional organic chain extender is a diisocyanate, diacid halide, or dicarboxy or diester substituted aliphatic or aromatic compound.

4. A molding powder according to Claim 1 wherein the polyfunctional polydiene prepolymer is dicarboxy 1,2-polybutadiene or dicarboxy 3,4-polyisoprene.

5. A molding powder according to Claim 4 wherein the polyfunctional organic chain extender is a diepoxide, diamine, dihydroxy, or diaziridine substituted aliphatic or aromatic compound.

6. A molding powder according to any of the preceding claims wherein the peroxide free radical initiator is an aliphatic or aromatic peroxide.

7. A molding powder according to Claim 2 wherein the prepolymer contains in addition to the polyfunctional polydiene, a polyfunctional polymeric material selected from polyesters, polyethers, and hydrocarbons.

8. A molding powder according to any of the preceding claims including a filler material selected from synthetic fabrics, carbon, asbestos, silica, glass, silicates, metals, metal oxides, and plastics materials.

9. A method for producing a molding powder according to Claim 1 which comprises reacting a liquid polymeric mixture containing polyfunctional prepolymers at least one of which is the said polyfunctional

polydiene with the polyfunctional chain extender and the peroxide free-radical initiator whereby an elastomeric material is formed, and comminuting the elastomeric material to a predetermined size.

10. A method for producing a molding powder according to Claim 1 which comprises mixing polyfunctional prepolymers of which at least one is the said polyfunctional polydiene with the polyfunctional organic chain extender and the peroxide free-radical initiator, placing the mixture in a heated extrusion press, extruding and reacting the mixture simultaneously to produce an elastomeric chain-extended material from which a hard resin may be subsequently produced by the application of heat, and cutting the extruded elastomeric material to a predetermined size.

11. A method for producing a molding powder according to Claim 1 which comprises spraying a liquid polymeric mixture containing polyfunctional prepolymers of which at least one is the said polyfunctional polydiene, the polyfunctional organic chain extender, and the peroxide free-radical initiator, into a drying chamber whereupon a chain extending reaction occurs to form minute discrete particles of elastomeric material having the peroxide molecularly disposed therethrough, and collecting the said discrete particles.

12. A method according to Claim 9, 10 or 11 wherein the polyfunctional polydiene is dihydroxy, 1,2-polybutadiene or dihydroxy 3,4-polyisoprene.

13. A method according to Claim 12 wherein the polyfunctional organic chain extender is a diisocyanate, diacid halide, or dicarboxy or diester substituted aliphatic or aromatic compound.

14. A method according to Claim 9, 10 or 11 wherein the polyfunctional polydiene is dicarboxy-1,2-polybutadiene or dicarboxy-3,4-polyisoprene.

15. A method according to Claim 14 wherein the polyfunctional organic chain extender is a diepoxide, diamine, dihydroxy, or diaziridine substituted aliphatic or aromatic compound.

16. A method according to any of Claims 9 to 15 wherein the peroxide free radical initiator is selected from the group consisting of aliphatic and aromatic peroxides.

17. A method according to Claim 9, 10 or 11 wherein the prepolymer contains in addition to the polyfunctional polydiene, a polyfunctional polymeric material selected from polyesters, polyethers, and hydrocarbons.

18. A method according to any of Claims 9 to 17 wherein a filler material selected from synthetic fabrics, carbon, asbestos, silica, glass, silicates, metals, metal oxides, and plastics materials is mixed into the liquid polymeric mixture.

19. A method of making a molded article which comprises preparing an elastomeric molding powder in accordance with any of Claims 9 to 18, placing the elastomeric powder in a suitable mold, and applying heat and pressure whereby the elastomeric material is cured to a hard, stiff, compact resin article.

20. A method according to Claim 19 wherein a filler material selected from synthetic fabrics, carbon, asbestos, silica, glass, silicates, metals, metal oxides, and plastics materials is mixed with the elastomeric powder prior to placing in the mold.

21. A molded article made by a method according to Claims 19 or 20.

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